Chemical species generated by high-vacuum ion gauges cause strong doping of graphene

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Outline

• Graphene doping

• Sources of doping in graphene

• Fabrication and characterization of CVD graphene

• Influence of ions on graphene doping

• Conclusion
Graphene doping


intrinsic  p-doped  n-doped
Source of doping: SiO$_2$ substrate

I=0.3nA  V=1.1V  Scale bar: 2.5 Å

I=1nA  V=1V  Scale bar: 0.1 nm

Peak-peak height variation: 2.5 nm  Scale bar: 2 nm

11/03/2013  (1) E. Stolyarova et al., PNAS, 104, 22, 9209 (2007); (2) M. Ishigami et al., Nano Letters, 7, 6, 1643 (2007)
Adsorption of molecules on graphene

- Exfoliated graphene
- Variable temperature insert
- $\mu = 5000\text{cm}^2/(\text{Vs})$
- Dirac peak at $V_{BG}=0$
- $\frac{\Delta \rho}{\rho} = \frac{\rho_0 - \rho}{\rho}$
  percental change of resistivity

11/03/2013 F. Schedin et al., Nat. Mater., 6, 652 (2007)
Sample fabrication: CVD graphene

1) 1000°C, 5 sccm H₂, 50 mTorr, 20 min
2a) 1035°C, 5 sccm H₂, 7 sccm CH₄, 120 mTorr, 4 min
2b) 1035°C, 5 sccm H₂, 7 sccm CH₄, 1 Torr, 15 sec
2c) Cooling, 5 sccm H₂, 7 sccm CH₄, 120 mTorr, 30 min
3) Spin 300 nm PMMA, leave 12 hs to dry
4) Etch graphene at back, oxygen plasma
5) Etch copper in Fe(NO₃)₃ solution
6,8,10) Rinse in DI water
7) H₂O/H₂O₂/HCl etch: remove metallic ions on sample
9) H₂O/H₂O₂/NH₄OH etch: remove insoluble organic solvents
11) Transfer on SiO₂ wafer, dry
12) 2nd layer of PMMA: reduction of wrinkles

11/03/2013 Liang et al., ACS Nano, 5, 11, 9144 (2011); Chr. Caillier et al., arxiv: 1302.5318v1, 21.02.2013
Big and small samples

- Some PMMA residues visible
- Small samples "etched" using a needle probe
- Reference sample for mobility measurement made of exfoliated graphene
Characterisation

Optical image

AFM image

Multilayer islands

Wrinkles
Vacuum chamber and ion gauge

(1) Chr. Caillier et al., arxiv: 1302.5318v1, 21.02.2013;
(2) http://www.lesker.com/newweb/Gauges/gauges_technicalnotes_1.cfm (28.02.2013)
Resistance measurements at various pressures

CVD graphene
\( \mu = 1000 \text{cm}^2/(\text{Vs}) \) as made
\( \mu = 1400 \text{cm}^2/(\text{Vs}) \) after current annealing

Exfoliated graphene
\( \mu = 1800 \text{cm}^2/(\text{Vs}) \) after current annealing

Current biased: 100 nA, 20 Hz
Lock-in voltage measurement

Significant increase in resistance only when ion gauge is on!
Time dependent doping

- From black to light blue: Ion gauge exposure time increased
- From light blue to black and insert: Exposure to air removes doping (measured 6 days after exposure to ion gauge)
Position dependent doping

Doping rate: $\frac{dn}{dt}$

$$n = \varepsilon_0 \varepsilon^* \hbar (d^* e)^* \Delta V_g$$

- All samples show pressure dependent doping rate
- Slope: $\alpha = 10^{14} \text{ cm}^2/(\text{s mbar})$
- Shaded region: ion gauge at different position
Conclusion

• Doping of graphene can be induced for example by
  • SiO₂ substrate
  • Adsorbed gas molecules
  • Ionized particles

• Graphene doping by ions is reversible if sample is exposed to air

• The smaller the ion gauge – sample distance, the higher the doping rate
Source of doping: H2O adsorption
Source of doping: PMMA

AFM images

(1) PMMA residues
   Roughness: 8Å
   No STM image with atomic resolution

(2) Cleaned surface (400°C, H₂/Ar, 1h)
   Roughness: 3Å
   STM image with atomic resolution